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AUTHOR(S):

Tsuji, Yasushi; Fujihara, Tetsuaki

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Carbon Dioxide as a Carbon Source in Organic Transformation: Carbon–Carbon Bond Forming Reactions by Transition-Metal Catalysts

Yasushi Tsuji* and Tetsuaki Fujihara

Recent carbon–carbon bond forming reactions of carbon dioxide with alkenes, alkynes, dienes, aryl zinc compounds, aryl boronic esters, aryl halides, arenes having acidic C–H bonds are reviewed in which transition-metal catalysts play an important role.

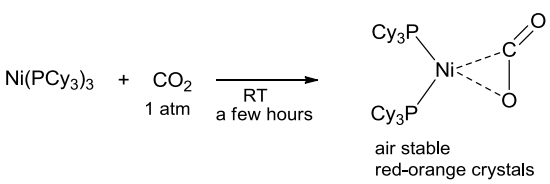
1. Introduction

Carbon dioxide (CO_2) is an ideal carbon source owing to its abundance, low cost, nontoxicity, and good potential as a renewable source.[1] However, it is not easy to activate such a thermodynamically and kinetically stable material. Therefore, catalysts must play an important role to develop useful transformations utilizing this attractive and environmentally friendly raw material. In this review article, recent progress on utilization of CO_2 in carbon–carbon bond forming reactions is surveyed. Such survey will offer basic idea to employ CO_2 as an attractive carbon source in organic transformations. There have been several excellent reviews on a similar subject.[2] On the other hand, carbon–oxygen bond and carbon–hydrogen bond forming reactions of CO_2 are also important for syntheses of organic carbonates (including CO_2/epoxide copolymerization), formic acid derivatives, and methanol. However, these reactions are not covered in the present article, since several useful reviews are available.[3d-g, 4e-h]

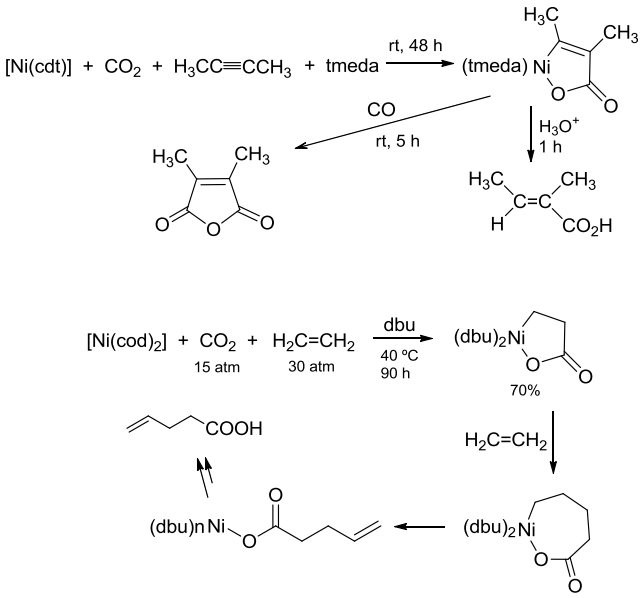
2. Stoichiometric reaction relevant to catalysis with CO_2

2.1 Transition metal complexes bearing CO_2

In order to develop efficient catalytic reactions, fundamental behaviours of CO_2 in the presence of a transition metal complex must be understood. As the first isolated and characterized metal CO_2 complex, Aresta et al. prepared $[Ni(CO_2)(PCy_3)_2]$ (Cy = cyclohexyl) complex in 1975 by treating $[Ni(PCy_3)_3]$ or $[\{Ni(PCy_3)_2\}_2N_2]$ with CO_2 in toluene. (Scheme 1).[5] The CO_2 coordinates to the electron rich Ni(0) centre as η^2 form. This finding suggested that CO_2 could be activated on a metal centre. More relevant to catalytic reactions of CO_2, Hoberg et al. found



Scheme 1 Synthesis of Ni(0) η^2-CO_2 complex.

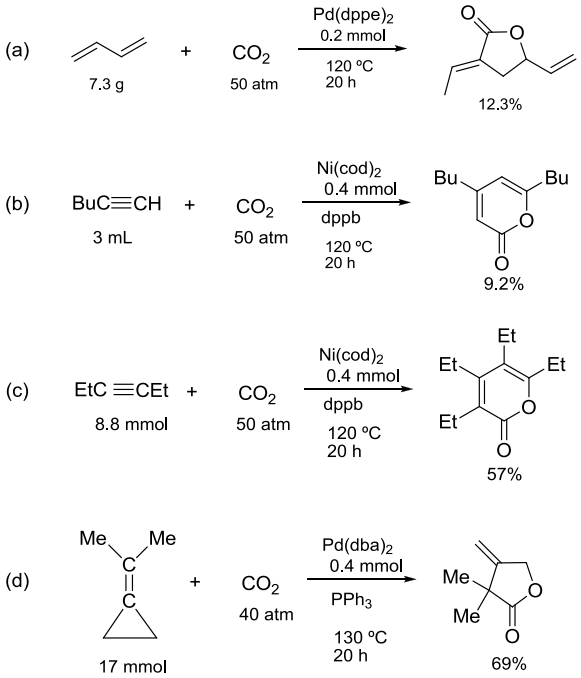


Scheme 2 Stoichiometric reaction of Ni(0) complex in the presence of 2-butyne and ethylene: cdt = 1,5,9-cyclododecatriene, tmeda = *N,N,N',N'*-tetramethylethylenediamine, dbu = 1,8-diazabicyclo[5.4.0]undec-7-ene

that CO_2 reacts with alkenes or alkynes in the presence of a stoichiometric amount of Ni(0) complexes to afford oxa-nickelacycles (Scheme 2).[6] Even the metal complexes were used in stoichiometric amounts, useful carbonyl compounds were obtained as products. Furthermore, a wide variety of complexes bearing CO_2 in various coordination styles (η^1, η^2, μ^2- η^2, μ^2- η^3, etc.) have been isolated and characterized to date.[7]

2.2 Seminal catalytic reactions of CO_2

A series of pioneering works for catalytic transformation of CO_2 with unsaturated compounds were carried out by Inoue et al. in 1976–1979.[8a-c] First, they reacted 1,3-dienes under a CO_2 pressure of 50 atm in the presence of a catalytic amount of $Pd(dppe)_2$ (dppe = $Ph_2(CH_2)_2PPh_2$) at 120 ºC (Scheme 3a).[8a] They found the lactone formed from CO_2 in a complex mixture of various products. In the presence of $Ni(cod)_2$—dppb (cod = 1,5-



Scheme 3. Early catalytic reactions of hydrocarbon unsaturates with CO_2. dppe = $Ph_2P(CH_2)_2PPh_2$, dppb = $Ph_2P(CH_2)_4PPh_2$, cod = 1,5-cyclooctadiene, dba = dibenzylideneacetone

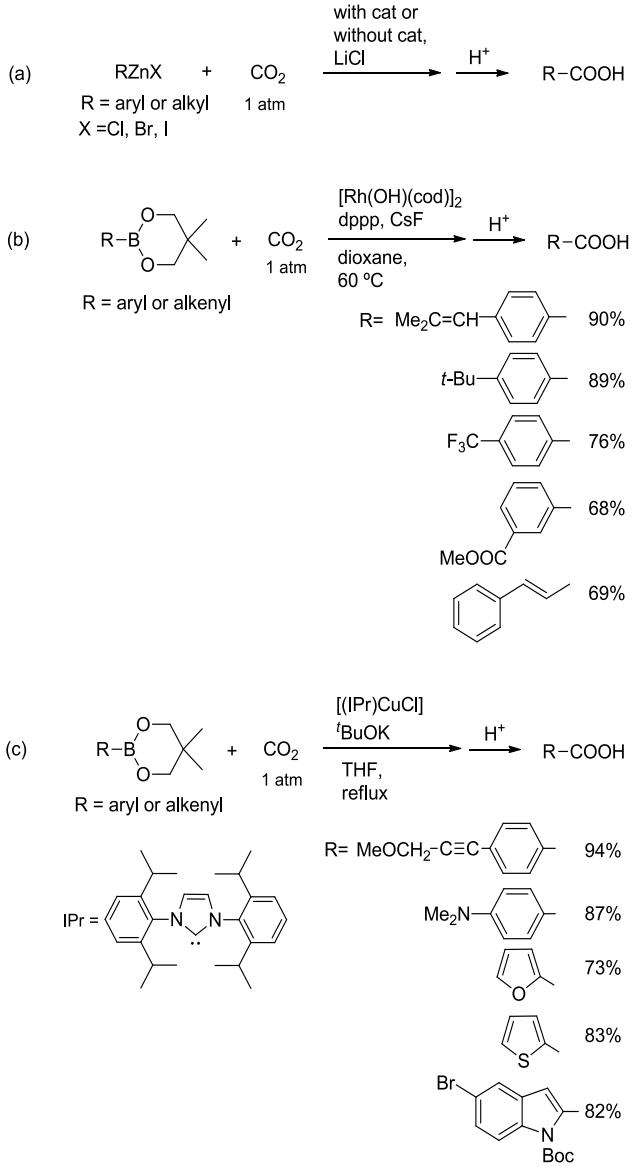
cyclooctadiene, dppb = $Ph_2P(CH_2)_4PPh_2$) as a catalyst at 120 ºC, two terminal alkynes reacted with CO_2 (50 atm) to afford lactones in only low yields (Scheme 3b).[8b] On the other hands, with the same catalyst system, internal alkynes provided the corresponding products in much higher yields (Scheme 3c).[8c] As for alkenes, Pd(0) catalyzed reaction of methylenecyclopropanes with CO_2 (40 atm) provided lactones successfully in good yields (Scheme 3c).[8d] In these reactions, yields of the products from CO_2 were not so satisfactory. However, these results clearly indicated that such catalytic reactions are very useful and promising.

3. Carbon-carbon bond forming reaction with CO_2

Carbon-carbon bond forming reactions are quite important to develop a wide variety of organic transformations employing CO_2. The most classical methods to realize the C-C bond forming reaction with CO_2 are the reaction with Grignard and organolithium reagents. Highly nucleophilic these reagents react with CO_2 without a catalyst. However, in these reactions, many useful functionalities such as ketones, esters, and nitriles are not tolerant. Thus, in order to develop transformations compatible with various functionalities, much less nucleophilic substrates must be employed. In such cases, catalysts are important and indispensable for successful C-C bond formation reactions with CO_2.

3.1 Reactions of Zinc compounds with CO_2

In place of Grignard and lithium reagents, less nucleophilic



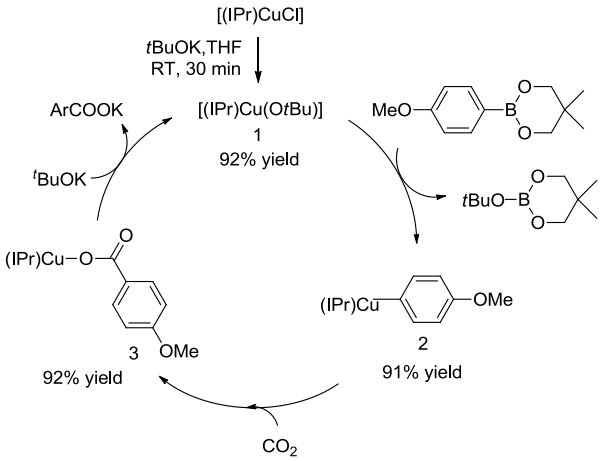
Scheme 4 Carboxylation reactions of organozinc and -borane compounds using CO_2

organozinc were utilized with CO_2 (Scheme 4a), since a wide variety of functionalities are compatible with organozinc compounds. Yorimitsu and Oshima reported that alkylzinc iodide–LiCl readily react with CO_2 in THF in the presence of $Ni(acac)_2$–PCy_3 as a catalyst to afford the corresponding carboxylic acids.[9a] They found that the addition of LiCl was essential for the carboxylation. They claimed that the Ni catalyst is indispensable for alkylzinc compounds, while PhZnI–LiCl reacted with CO_2 in THF without the Ni catalyst to afford benzoic acid in 36% yield. Independently, Dong et al reported that carboxylation of arylzinc bromides with CO_2 proceeded in the presence of a similar Ni and Pd catalysts bearing PCy_3 as a ligand.[9b] They reported that no carboxylation occurred without the transition metal catalyst. On the other hand, Kondo et al found that transition metal catalysts are not necessary for these

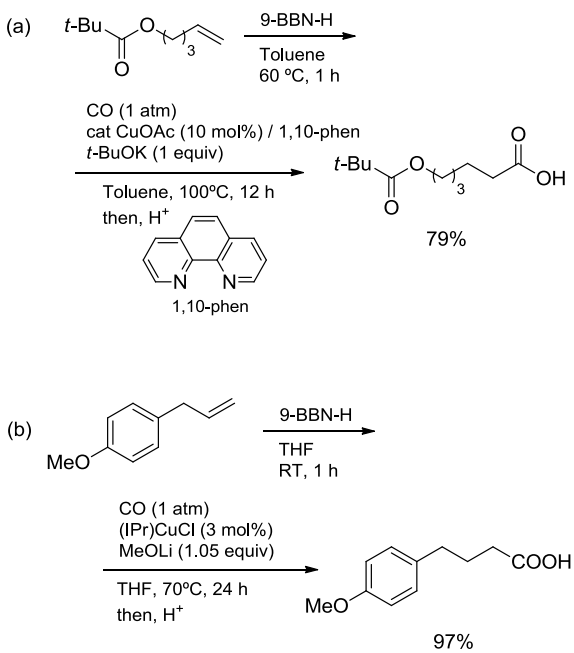
reactions, but only 2.8 equiv of LiCl in DMF is sufficient for the reaction.[9c] Activities of organozinc compounds seem to be varied considerably depending on reaction conditions, and some reactions really proceed without a transition metal catalyst.

3.2 Reactions of organoboronic esters with CO_2

Organoboron compounds are easily prepared by various methods and are highly useful substrates in a variety of organic synthesis. Iwasawa et al. reported that aryl- and alkenylboronic esters react with CO_2 in the presence of $[Rh(OH)(cod)]_2$ (3

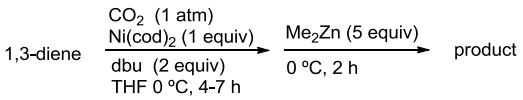


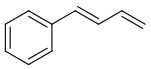
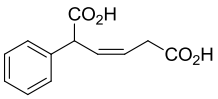
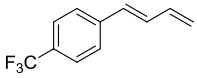
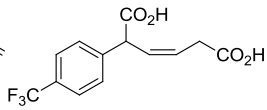
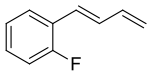
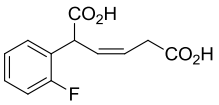
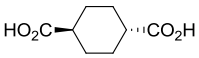
Scheme 5 Possible catalytic cycles and isolation of catalytic species in Scheme 4c



Scheme 6 Formal reductive carboxylation of terminal alkenes via hydroboration

Table 1 Nickel-mediated 1,4-double-carboxylation of 1,3-diene



1,3-diene	product	yield (%)
		68
		75
		73
		50

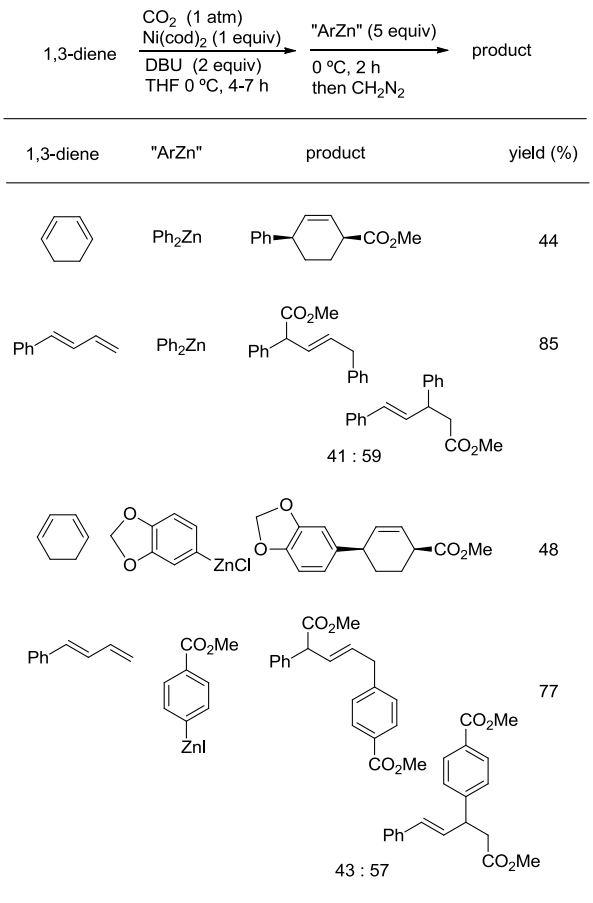
mol%), dppp ($Ph_2P(CH_2)_4PPh_2$, 7 mol%), and CsF (3 equiv) to provide the corresponding carboxylic acids in high yields (Scheme 4b).[10a] In the reaction, ester part of the boronic esters affected the carboxylation considerably. Actually, only 2,2-dimethyl-1,3-propanediolate ester (Scheme 4b) afforded the carboxylation products in high yields, while other propan1,3-diolate, ethylene glycolate, pinacolate, and catecholate gave almost no products. On the other hand, insertion of CO_2 into carbon-Cu bonds has been known.[11] Hou et al. reported that the same carboxylation of organoboronic esters are possible with N-heterocyclic carbene copper catalysts, in which the same effect of the ester moiety was observed (Scheme 4c).[10b] Importantly, most copper catalytic species (**2** and **3** in Scheme 5) were isolated in high yields (91% and 92%) and fully characterized including X-ray crystal structure analysis. The mechanism shown in Scheme 5 was supported by DFT calculations indicating insertion of CO_2 into the Cu-Ar bond is the rate-determining step in which nucleophilic attack of the aryl moiety on CO_2 affords the new C – C bond.[10c] Iwasawa et al. reported similar carboxylation by a copper catalyst.[10d]

Sawamura et al. (Scheme 6a)[12a] and Hou et al. (Scheme 6b)[12b] independently found that the copper catalyzed carboxylation of alkylboranes were carried out via hydroboration of terminal alkenes with 9-borabicyclo[3.3.1]nonane (9-BBN-H). The overall process represents a useful reductive carboxylation of terminal alkenes with CO_2.

3.3 Carboxylations of dienes and alkenes

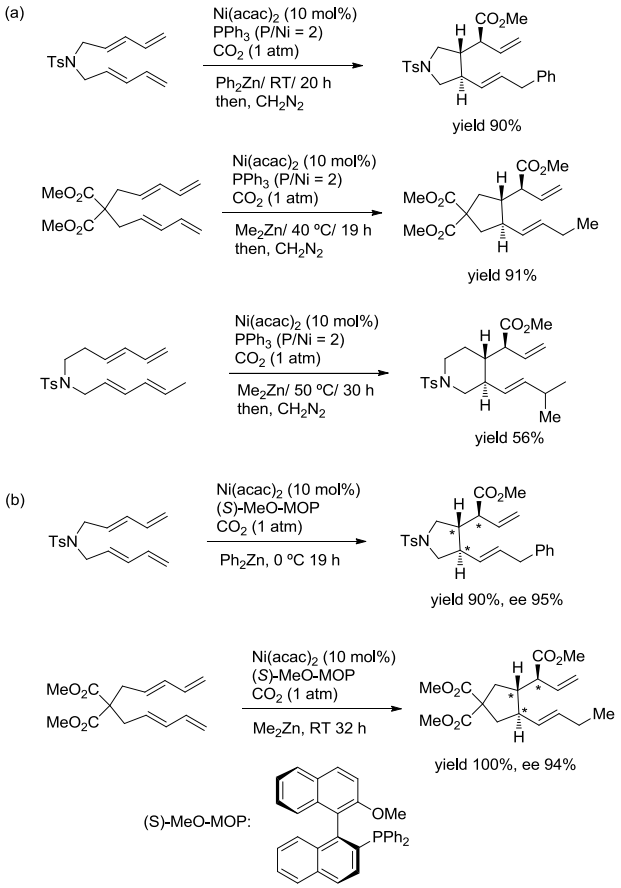
Mori et al. developed carboxylation of 1,3-dienes and allenes with CO_2 via allylnickel intermediates.[13] When 1,3-dienes were reacted with 1 equiv of $Ni(cod)_2$ and 2 equiv of dbu under CO_2,

Table 2 Nickel-mediated arylative mono-carboxylation of 1,3-diene

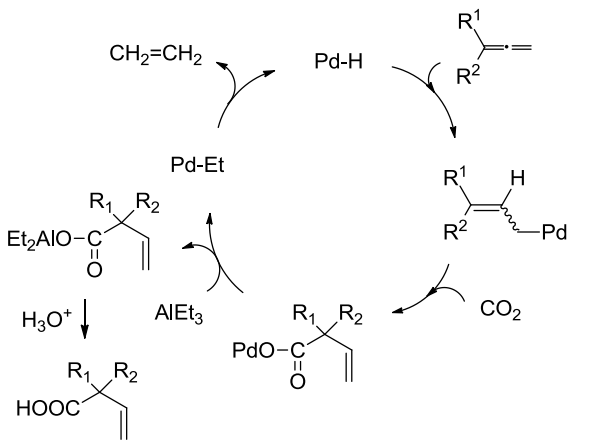


and then further with 5 equiv of Me_2Zn, 1,4-*double*-carboxylation products were afforded in good yields (Table 1).[13a] Although the mechanism of the stoichiometric reaction was not clear, the two CO_2 molecules, but no Me moieties, were incorporated in the products. In contrast, when aryl zinc reagents (ArZn) instead of Me_2Zn were employed in the similar stoichiometric reaction, arylative mono-carboxylation proceeded (Table 2).[13a] Furthermore, by using bis-1,3-dienes as the substrates, the catalytic reaction provided ring-closing carboxylated products regio- and stereoselectively in high yields (Scheme 7a).[13b] The asymmetric carbonylative cyclization were realized under similar reaction conditions with chiral phosphine ligands (Scheme 7b).[13c] Mori et al. also found Ni-catalyzed double-carboxylation of trimethylsilylallene with CO_2[13d] and Ni-promoted carboxylation/cyclization cascade reaction of allenyl aldehydes.[13e] In the former case, the silyl moieties were indispensable for the double carboxylation.

Iwasawa et al. reported hydrocarboxylation of allenes with CO_2 catalyzed by Pd pincer catalyst (Table 3).[14a] $AlEt_3$ was employed as a reducing agent and a hydrido source after the β-hydride elimination of the resulting ethyl palladium intermediate (Scheme 8). With a similar Pd catalyst system, one-to-one coupling of 1,3-dienes with CO_2 occurred (Table 4).[14b]

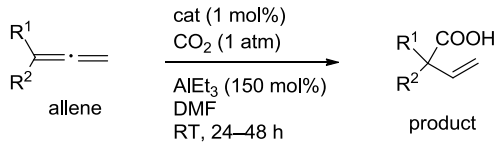


Scheme 7 Nickel-catalyzed ring-closing carboxylation of bis-1,3-dienes

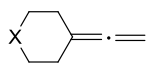


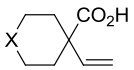
Scheme 8 Catalytic cycle of Pd-catalyzed hydrocarboxylation of allenes

Table 3 Pd-catalyzed hydrocarboxylation of allenes



allene	yield of product
R^1=Me, R^2=Me	95%
R^1=Me, R^2=Ph	73%
R^1=Me, R^2= -$(CH_2)_2$CH=CMe_2	85%





72%
89%
63%
84%

cat:

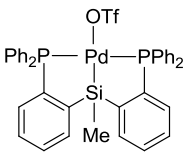
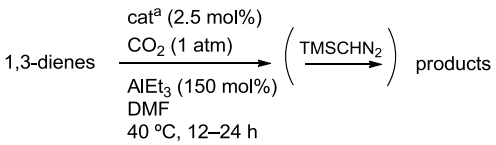
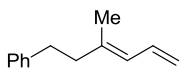
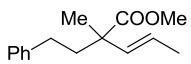
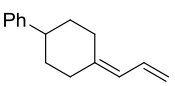
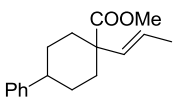
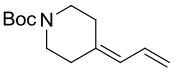
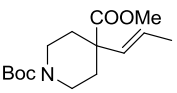
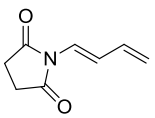
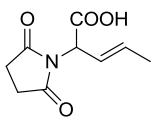
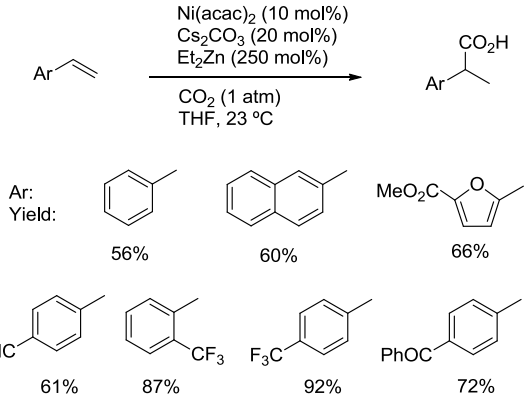


Table 4 Pd-catalyzed hydrocarboxylation of 1,3-diene: one-to-one coupling with CO_2

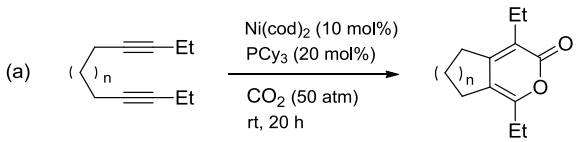


1,3-dienes	products	yields (%)
		79
		92
		79
		81

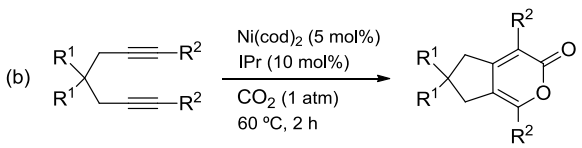
[a] The same Pd complex in Table 3 was used as a catalyst



Scheme 9 Ni-catalyzed reductive carboxylation of styrenes using CO_2



n = 1 88%
n = 2 85%



R^1 = CO_2Me, R^2 = Me: 93%
R^1 = CO_2Me, R^2= *i*Pr: 86%
R^1 = $PhCH_2OCH_2$, R^2=Me: 93%

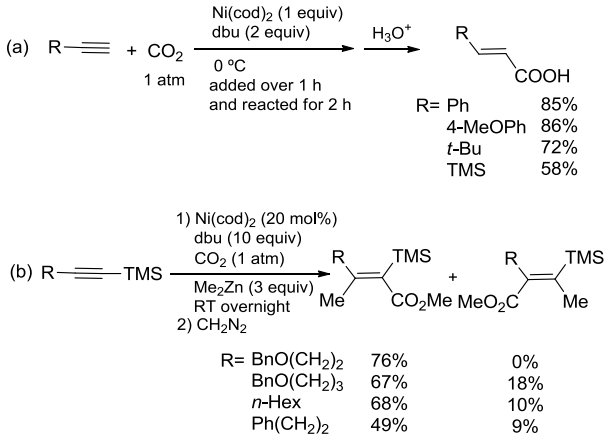
Scheme 10 Carboxylation of α,ω-diynes with CO_2

As for alkenes, Rovis et al. found reductive carboxylation of styrene derivatives with Et_2Zn and CO_2 (Scheme 9).[15] They proposed an insertion on Ni-H into carbon-carbon double bonds of styrenes followed by insertion of CO_2, rather than the Hoberg's metallacycle shown in Scheme 2.

3.4 Carboxylation of alkynes

Pioneering works for catalytic carboxylation of alkynes were carried out by Inoue et al. as shown in Scheme 3b,c.[8b,c] Tsuda and Saegusa found that the reactions of α,ω–diynes under pressurized CO_2 (50 atm) in the presence of Ni-phosphane catalyst proceeded smoothly and afforded bicyclic α-pyrones in good yields (Scheme 10a).[16a] In this transformation, IPr ligand in place of phosphanes is much more effective and provided the similar carboxylated products in high yields under 1 atm of CO_2 (Scheme 10b).[16b]

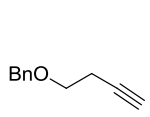
On the other hand, Yamamoto et al. reported that terminal alkynes reacted with 1 equiv of $Ni(cod)_2$ and 2 equiv of dbu



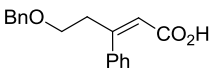
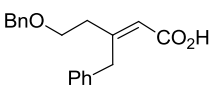
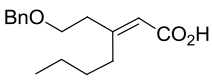
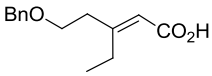
Scheme 11 Carboxylation of terminal and TMS acetylenes

under CO_2 (1 atm) at 0 ºC in a highly regio- and chemoselective manner (Scheme 11a).[17a] Similar carboxylation reaction with 1 equiv of $Ni(cod)_2$ was also carried out using bidentate amidine ligands.[17b] When alkyl or aryl zinc reagent was added into the Yamaoto's system, alkylative and arylative carboxylation of alkynes proceeded (Table 5).[17c,e] Interestingly, BuZn reagent afforded the butylated product (entry 3), while EtZn gave hydrocarboxylated product via β-hydride elimination (entry 4). This alkylative carboxylation could be carried out catalytically when trimethylsilyl acetylenes were employed as substrates

Table 5 Carboxylation of alkyne with $Ni(cod)_2$ and organozinc reagents



CO_2 (1 equiv)
$Ni(cod)_2$ (1 equiv)
DBU (2 equiv)
THF, 0 ºC, 1 h
"RZn"
0 ºC, 2 h
product

entry	"RZn"	equiv	yield (%)[a]	product
1	PhZnCl	2	69	
2	$PhCH_2ZnCl$	1.5	81	
3	BuZnI	3	68	
4	Et_2Zn	1.5	9[b]	

[a] Isolated yield based on $Ni(cod)_2$

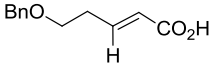
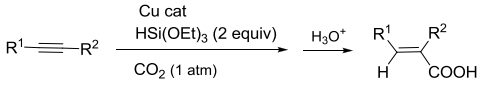
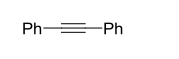
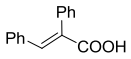
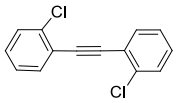
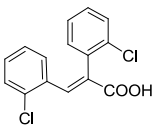
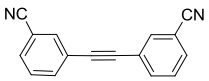
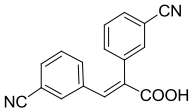
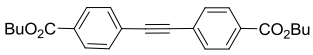
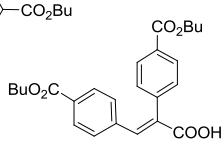
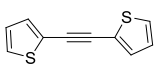
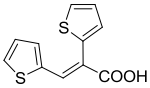
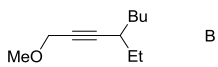
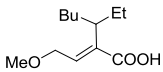
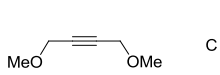
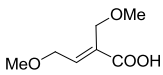
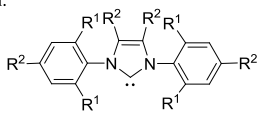
[b]  in 78% yield

Table 6 Cu-catalyzed hydrocarboxylation of alkyne using CO_2 and hydrosilanes



alkyne	conditions[a]	product	isolated yield (%)
	A		72
	A		64
	A		52
	A		64
	A		78
	B		74
	C		66

[a] Conditions A: IMesCuF (1–2 mol%) in 1,4-dioxane at 100 ºC for 12 h. Conditions B: ClIPrCuF (2.5 mol%) in hexane at 70 ºC for 14 h. Conditions C: IPrCuF (2.5 mol%) in 1,4-dioxane at 100 ºC for 14 h.



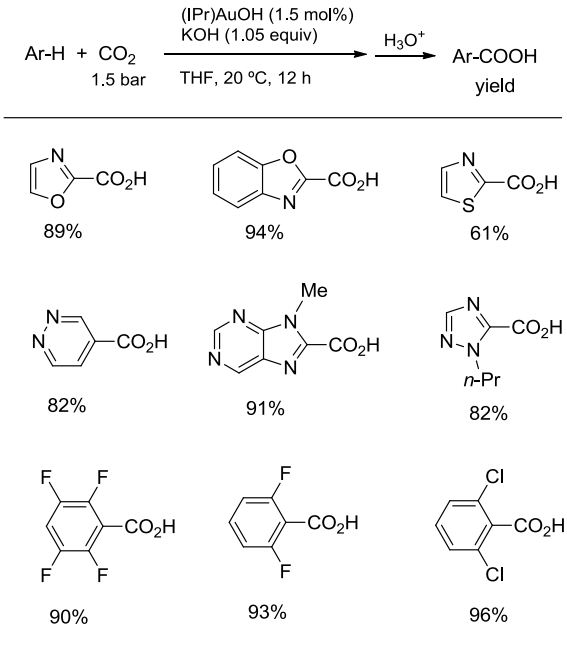
IMes: R^1=R^2=Me, R^3=H
ClIPr: R^1=*i*Pr, R^2=H, R^3=Cl

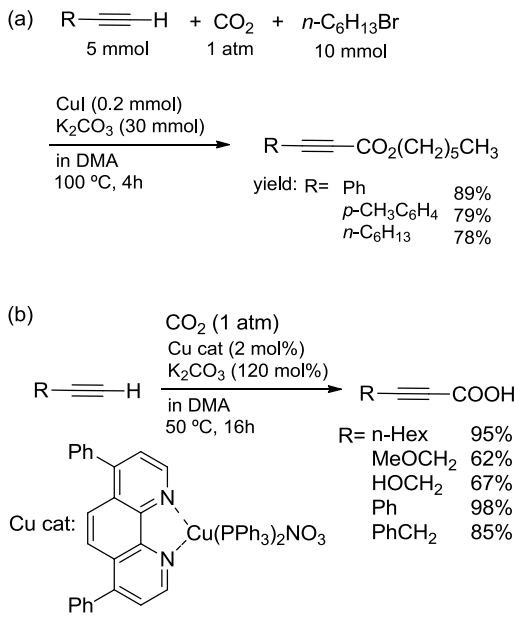
(Scheme 11b).[17d]

In order to utilize CO_2 in C-C bond formations, reducing reagents have been indispensable in the reactions. To date, highly reactive and pyrophoric reagents such as Et_2Zn[9,15,17a,d,e] and Et_3Al[14] were employed in stoichiometric and catalytic reactions. We recently reported that hydrosilanes, more mild and easy-to-handle reducing reagents, can be used in Cu catalyzed hydrocarboxylation of alkynes.[18a] Various alkynes were hydrocarboxylated efficiently using $HSi(OEt)_3$ in good yields (Table 6). In the reactions, $HSi(OEt)_3$ could be replaced with polymethylhydrosiloxane (PMHS), which is a cheap by-product of the silicon industry. Ma et al. found that the same reaction proceeded with $Ni(cod)_2$-CsF as a catalyst and Et_2Zn as a reducing reagent.[18b] Ma also reported methylative carboxylation of homopropargylic alcohols.[18c]

Inoue et al. found that terminal alkynes reacted with

Table 7 Au-catalyzed carboxylation of aromatic C-H bonds





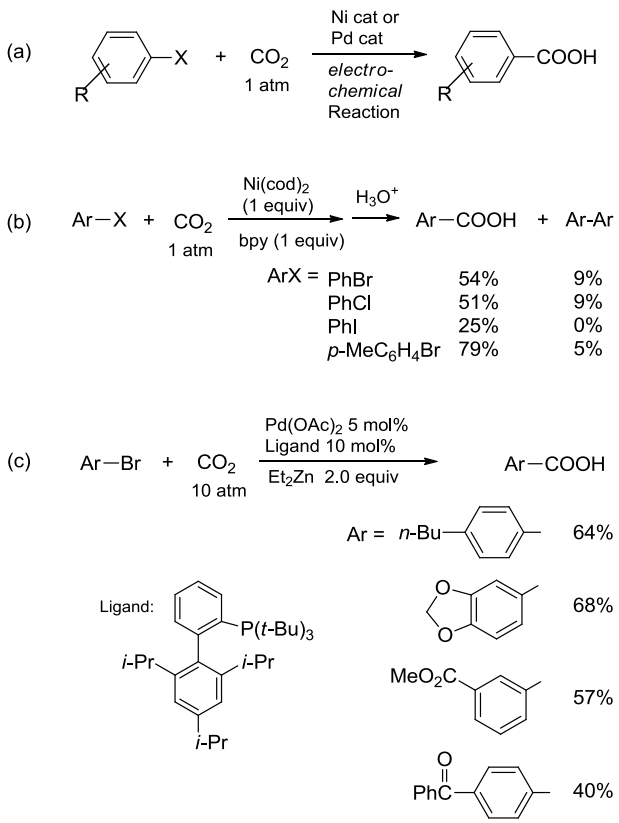
Scheme 12 Carboxylation of terminal alkynes with CO_2 with and without bromoalkanes

bromoalkanes under CO_2 in the presence of a catalytic amount of CuI.[19a] Insertion of CO_2 into the acetylenic C-H bonds to give alkyl 2-alkynoates at 100 °C in good yields (Scheme 12a). CuBr, AgI, or $AgNO_3$ can be utilized as the catalyst successfully. This reaction was applied to one-pot synthesis of arylnaphthalene lactones.[19b] Recently, IPrCuCl was found to be a more efficient and the reaction proceeded even at lower temperature (60 °C).[19c] Furthermore, insertion of CO_2 into the C-H bond proceeded without bromoalkanes in the presence of a Cu[20a,b] (Scheme 12b) or Ag[20c] catalyst. The same reactions could be carried out without the transition metal catalysts at 120–160 °C, but 2 equiv of Cs_2CO_3 was indispensable.[20d]

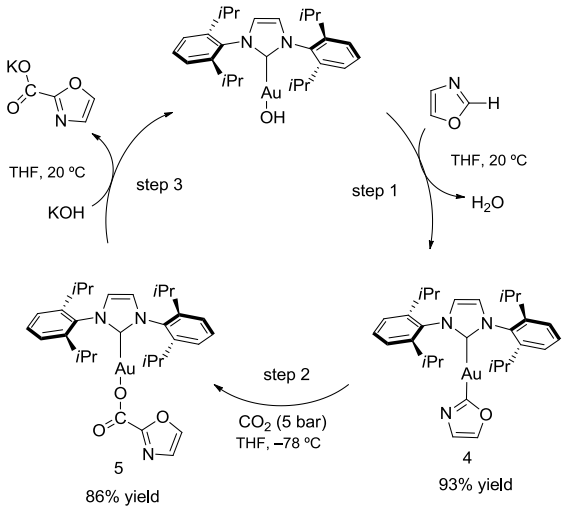
3.5 Carboxylation of aryl halides

As mentioned earlier, the carboxylation reactions of arylzinc (section 2.1) and arylboronic esters (section 2.2) with CO_2 have been studied intensively, since in these reactions various functionalities that are compatible unlike with Grignard reagents. However, these zinc and boron compounds must be prepared from the corresponding aryl halides prior to the catalytic reactions. Thus, the direct carboxylation of the parent aryl halides is most desirable as this is a more straightforward transformation.

The catalytic carboxylation of aryl halides employing CO_2 was first developed as *electrochemical* reactions in the presence of nickel[21a-c] and palladium catalysts (Scheme 13a).[21d,e] Unfortunately, these were not efficient synthetic methods, and the scope of possible substrates was quite restricted. Later, the non-electrochemical carboxylation of aryl bromides and chlorides using CO_2 was carried out in the presence of *stoichiometric* amounts of Ni(0) complexes and 2,2'-bipyridine (bpy) (Scheme 13b).[22a] Recently, the carboxylation of aryl bromides employing CO_2 was performed *catalytically* using a palladium complex as the catalyst.[22b]



Scheme 13 Carboxylation of aryl halides with CO_2



Scheme 14 Stoichiometric reactions relevant to the catalytic cycle

3.6 Carboxylation of arenes having acidic C-H bonds

The Kolbe-Schmitt salicylic acid synthesis from sodium phenolate and CO_2 is an early example of carboxylation of C–H bonds. Such direct carboxylation of C–H bonds must be more sustainable transformations. Recently, Nolan et al. reported that (IPr)AuOH can perform the activation of C–H bonds of electron-deficient arenes.[23a] They found that the same Au(I) complex is very active for carboxylation of aromatic acidic C-H bonds (p*Ka* values < 30) with CO_2 (Table 7).[23b] The possible catalytic cycle for the present C-H carboxylation (Scheme 14) is similar to the mechanism postulated for Cu(I) catalyzed carboxylation of organoboronic esters (Scheme 5). The authors confirmed the mechanism by stoichiometric reactions (Scheme 14). Protonolysis of (IPr)AuOH by 1 equiv of oxazole gave the intermediate **4**, which was isolated in 93% yield (step 1). Reaction of **4** by saturating the solution with CO_2 at –100 ºC afforded carboxylate complex **5** in 86% isolated yield (step 2). Finally, (IPr)AuOH was regenerated upon metathesis of **5** with 1 equiv of KOH with precipitation of potassium oxazole-2-carboxylate (step 3). Hou et al.[23c] and Nolan and coworkers[23d] independently reported that Cu catalysts are active as catalysts in the carboxylation reaction of the acidic C–H bonds (Table 8).[23c] Hou isolated catalytic intermediates (arylcopper and copper carboxylate) in a stoichiometric reaction and determined the structures by X-ray crystallographic analysis.[23c] However, these C–H carboxylations could proceed with only a base (Cs_2CO_3 is most suitable) at 125 ºC.[23e] Iwasawa et al. found the first C–H carboxylation with CO_2 via chelation-assisted C–H activation. Various 2-arylpyridines and 1-arylpyrazoles afforded carboxylated products in the presence of a Rh catalyst and a stoichiometric amount of $AlMe_2(OMe)$ (Table 9).

Table 8 Cu-catalyzed carboxylation of aromatic C-H bonds

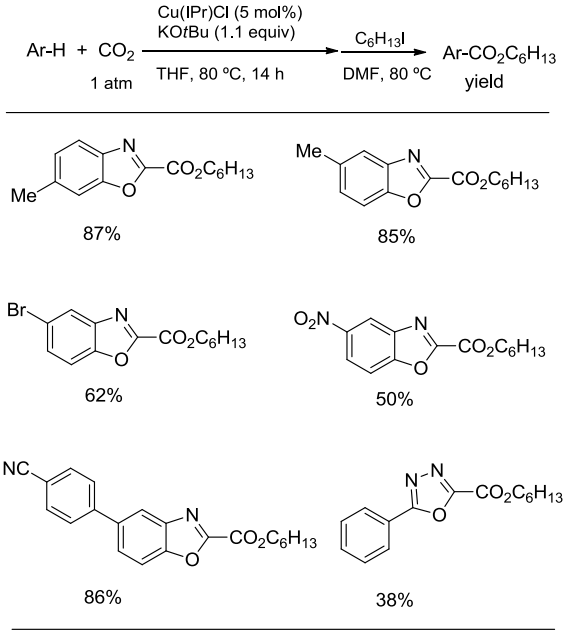
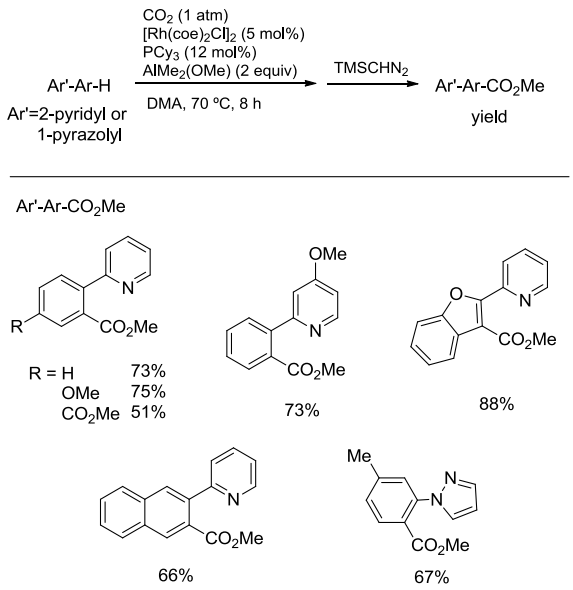


Table 9 Rh-catalyzed direct carboxylation of arenes via chelation-assisted C–H bond activation



Conclusions

Carbon dioxide (CO_2) can be utilized in carbon–carbon bond forming reactions with the aid of transition-metal catalysts. Organozinc compounds usually do not react with CO_2 without a transition-metal catalyst. and Ni and Pd catalysts are active to

afford the corresponding carboxylic acids. Organoboronic esters are also useful substrates which are reacted with CO_2 to provide the carboxylic acids in the presence of Rh and Cu catalysts. In the Cu-catalyzed reaction, aryl-Cu or ArCOOCu intermediates were isolated and fully characterized. Dienes, alkenes, and alkynes were efficiently reacted with CO_2 in the presence of Ni, Pd, and Cu catalysts. Usually, highly reactive and pyrophoric reducing reagents such as Et_2Zn and Et_3Al are indispensable in the reactions. Recently, easy-to-handle hydrosilanes such as $HSi(OEt)_3$ and polymethylhydrosiloxane (PMHS) can be employed with a Cu catalyst. Carboxylation of aryl halides and arenes having acidic C–H bonds are realized.

Notes and references

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, 615-8510, Japan. Fax:+81-75-383-2514; Tel:+81-75-383-2515; E-mail: ytsuji@scl.kyoto-u.ac.jp

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Yasushi Tsuji was born in Japan (Osaka) in 1953. He received his Bachelor (1976), Master (1978), and Doctor of Engineering (1981) form Kyoto University under the supervision of Professor Yoshinobu Takegami. He was appointed as a Research Associate at the Faculty of Engineering, Kyoto University in 1981. He spent the year 1986 to 1987 as a Postdoctoral Fellow at Northwestern University with Professor Tobin J. Marks. He was an Associate Professor at the Faculty of Engineering, Gifu University from 1989 to 1998, then at the Institute for Molecular Science from April to September in 1998. He was promoted to a Full Professor at the Catalysis Research Center, Hokkaido University in 1998. In 2006, he moved back to Kyoto and has been a Full Professor at the Faculty of Engineering, Kyoto University. He received the Chemical Society of Japan Award for Creative Work in 2002. He has been interested in the development of new catalysis by transition -metal complexes.

Tetsuaki Fujihara was born in Japan (Shiga) in 1973. He received his Bachelor of Science from Shizuoka University in 1996. He moved to Hokkaido University, where he pursued his Master of Science (1998). He received his Ph.D. degree in 2001 from Hokkaido University under the supervision of Prof. Yoichi Sasaki and Prof. Taira Imamura. Subsequently, he conducted a postdoctoral research with Prof. Koji Tanaka at Institute for Molecular Science. In 2004, he joined to Prof. Yasushi Tsuji's group at Catalysis Research Center, Hokkaido University as a postdoctoral fellow. He was appointed an Assistant Professor at Kyoto University in 2006. His research interests are related to synthesis of nano-scale molecular catalysts as well as development of novel organic transformation catalyzed by transition-metal complexes.